

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-068149

(43)Date of publication of application : 16.03.2001

(51)Int.Cl.

H01M 10/36

H01M 4/02

H01M 4/58

(21)Application number : 11-244040

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(22)Date of filing : 30.08.1999

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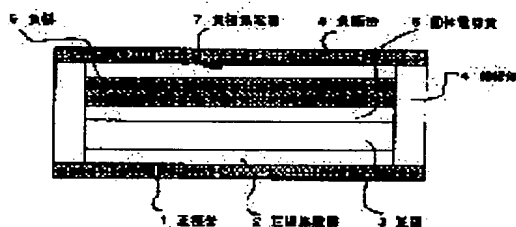
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## (54) ALL SOLID LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To relax remaining stress according to lithium ion diffusion within solid electrolyte particles, eliminate deterioration in internal resistance over a long period of time, and provide a battery with small capacity deterioration.

SOLUTION: A lithium secondary battery assembled by interposing a solid electrolyte 5 between a positive electrode and a negative electrode both made of an active material and sealing them in an outer package has the solid electrolyte made of a sintered body containing a lithium transition metal composite oxide having at least one kind of layer structure of  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$ , and  $\alpha\text{-LiAlO}_2$ .



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision  
of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package, and they are  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$ , or  $\alpha\text{-LiAlO}_2$  about said solid electrolyte. All solid-state lithium secondary batteries characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.

[Claim 2] In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq x \leq 1.2)$   $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure While forming with a sintered compact  $(1.0 \leq x \leq 1.2, 0.4 \leq y < 0.6)$  They are  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  of spinel type structure, or  $(1.25 \leq x \leq 1.40)$   $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  about said negative electrode. All solid-state lithium secondary batteries characterized by forming with a sintered compact  $(1.25 \leq x \leq 1.40)$ .

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to all the solid-state lithium secondary batteries that pinch a solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and are enclosed with it in a sheathing package about all solid-state lithium secondary batteries.

[0002]

[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device, and the cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.

[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.

[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has a problem of the rise of the internal resistance by a liquid spill of the electrolytic solution or deposit of the electrolytic-solution decomposition product in an active material front face.

[0005] In order to solve such a problem, development of all the solid-state lithium secondary batteries that do not use any electrolytic solution is considered.

[0006] JP,6-111831,A -- MnO<sub>2</sub> or a lithium compound is reacted to the front face of the positive electrode which consists of an alkali-metal manganese multiple oxide -- making -- Li<sub>2</sub>MnO<sub>3</sub> of a solid electrolyte Making it generate is advocated. According to this approach, since the adhesion of a positive electrode and a solid electrolyte is good, there is an advantage that interfacial resistance is low.

[0007] However, Li<sub>2</sub>MnO<sub>3</sub> Since it acts also as an active material which has charge and discharge potential in the 3V neighborhood, the very thing may check the charge-and-discharge reaction of a positive electrode, and the expansion contraction by the ejection and insertion of a lithium ion may also produce destruction of solid-state structure from a certain thing in that case, and, at this rate, it cannot serve as a solid electrolyte which can be used over a long period of time.

[0008] Furthermore, by JP,6-111831,A, when using a solid electrolyte, and an active material carries out expansion contraction at the time of the charge and discharge of an indispensable place, the method of avoiding the danger that the contact in the interface of an electrode and a solid electrolyte will be lost is not stated.

[0009] Moreover, in JP,6-275314,A, while using transition-metals oxide as a positive electrode, the lithium secondary battery which consists of a sulfide system lithium ion conductivity solid electrolyte with the ionic conductivity of bulk higher than an oxide system lithium ion conductivity solid electrolyte as a solid electrolyte is advocated.

[0010] However, since oxygen and the moisture of a minute amount decompose and a sulfide loses the work as a solid electrolyte, it has the fault that it can be hard to obtain a reliable cell.

[0011] This invention is made in view of the trouble of such a conventional technique, a solid

electrolyte and an electrode carry out expansion contraction, and contact of the interface of a solid electrolyte and an electrode is spoiled, and it aims at offering all the solid-state lithium secondary batteries that canceled the conventional trouble that a solid electrolyte decomposed with oxygen and the moisture of a minute amount.

[0012]

[Means for Solving the Problem] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material in all the solid-state lithium secondary batteries concerning claim 1, and was enclosed with it in the sheathing package in order to attain the above-mentioned purpose, and they are  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$ , or  $\alpha\text{-LiAlO}_2$  about said solid electrolyte. It is characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.

[0013] moreover, in all the solid-state lithium secondary batteries concerning claim 2 In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq X \leq 1.2) \text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure While forming with a sintered compact  $(1.0 \leq X \leq 1.2, 0.4 \leq Y < 0.6)$  They are  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  of spinel type structure, or  $(1.25 \leq X \leq 1.40) \text{Li}_x\text{Ti}_{2-x}\text{O}_4$  about said negative electrode. It is characterized by forming with a sintered compact  $(1.25 \leq X \leq 1.40)$ .

[0014]

[Embodiment of the Invention] Hereafter, the operation gestalt of invention concerning each claim is explained. the sectional view showing the example of a configuration of all the solid-state lithium secondary batteries of invention which drawing 1 requires for claim 1 and claim 2 -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [ a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8 ] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.

[0015] In a solid electrolyte 5, it is  $\text{Li}_2\text{MnO}_3$ . Or  $\text{Li}_2\text{TiO}_3$  Or  $\alpha\text{-LiAlO}_2$  It uses. This solid electrolyte has the layer structure of a rock salt mold.

[0016] as the raw material which constitutes (1) solid-electrolyte fine particles or a solid electrolyte in order to produce a solid electrolyte 5 --  $\text{LiOH}$ ,  $\text{LiOH-H}_2\text{O}$ , and  $\text{Li}_2\text{CO}_3$  etc. -- with a lithium compound titanium compounds, such as manganese compounds, such as  $\text{MnO}$ ,  $\text{MnO}_2$ , and  $\text{MnOOH}$ , or  $\text{TiO}_2$ , or aluminum  $2\text{O}_3$  etc. -- with an aluminium compound How to judge and sinter, after distributing the water or the organic solvent in which the shaping assistant was dissolved, adjusting a slurry, carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) solid electrolytes or a solid electrolyte, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0017] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0018] The active material which consists of  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq X \leq 1.2) \text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure  $(1.0 \leq X \leq 1.2, 0.4 \leq Y < 0.6)$  is used for a positive electrode 3.

[0019] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if X of  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$   $(1.05 \leq X \leq 1.2)$  is smaller than 1.05, and X is larger than 1.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode will be spoiled.

[0020] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and  $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$   $(1.0 \leq X \leq 1.2, 0.4 \leq Y < 0.6)$  will generate an impurity phase if sufficient high potential will not be obtained as compared with  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$   $(1.05 \leq X \leq 1.2)$  if this Y is smaller than 0.4, and Y becomes 0.6 or more, it is not desirable.

[0021] The active material which consists of  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  of spinel type structure or  $(1.25 \leq X \leq 1.40) \text{Li}_x\text{Ti}_{2-x}\text{O}_4$   $(1.25 \leq X \leq 1.40)$  is used for a negative electrode 6. The

effectiveness of suppressing the expansion contraction at the time of charge and discharge if  $X$  of  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  or  $(1.25 \leq X \leq 1.40) \text{Li}_x \text{Ti}_{2-x} \text{O}_4$  ( $1.25 \leq X \leq 1.40$ ) is smaller than 1.25 here is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if  $X$  is larger than 1.4, it is not desirable.

[0022] The raw material which constitutes (1) active material, a solid electrolyte, or a solid electrolyte in order to produce a positive electrode 3 and a negative electrode 6, Distribute the water or the organic solvent in which the electric conduction agent and the shaping assistant were dissolved, and a slurry is adjusted. How to judge and sinter, after carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) active materials, a solid electrolyte, or a solid electrolyte, and an electric conduction agent, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0023] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0024] as the electric conduction agent added by a positive electrode 3 and the negative electrode 6 --  $\text{WO}_3$  etc. -- it is.

[0025] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material or a solid electrolyte, an active material, or a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.

[0026] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of electroconductive glue which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, contained conductive particles, such as gold, silver, copper, aluminum, nickel, and conductive carbon.

[0027] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as a terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0028] In order that the insulating section 4 may prevent the internal short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0029] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.

[0030]

[Example 1] as positive active material --  $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  as a 3wt(s)% and electric conduction agent --  $\text{WO}_3$  7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material --  $\text{Li}_{1.33} \text{Mn}_{1.67} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  as a 3wt(s)% and electric conduction agent --  $\text{WO}_3$  7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0031] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of  $\phi 10\text{mm}$  and thickness ] 100 micrometers.

[0032]

[Example 2] as positive active material --  $\text{Li}_{1.0} \text{Ni}_{0.5} \text{Mn}_{1.5} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  as a 3wt(s)% and electric conduction agent --  $\text{WO}_3$  7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material --  $\text{Li}_{1.33} \text{Ti}_{1.67} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{TiO}_3$  as a 3wt(s)% and electric conduction

agent -- WO<sub>3</sub> 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0033] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0034] (What has what kind of the layer structure ?)

[0035]

[Example 3] as positive active material -- Li<sub>1.1</sub> Mn<sub>1.9</sub>O<sub>4</sub> as 90wt(s)% and a solid electrolyte -- Li<sub>2</sub> MnO<sub>3</sub> as a 3wt(s)% and electric conduction agent -- WO<sub>3</sub> 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li<sub>2</sub> TiO<sub>3</sub> 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li<sub>1.33</sub>Mn<sub>1.67</sub>O<sub>4</sub> as 90wt(s)% and a solid electrolyte -- Li<sub>2</sub> MnO<sub>3</sub> as a 3wt(s)% and electric conduction agent -- WO<sub>3</sub> 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0036] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0037]

[Example 4] as positive active material -- Li<sub>1.0</sub> nickel<sub>0.5</sub> Mn<sub>1.5</sub>O<sub>4</sub> as 90wt(s)% and a solid electrolyte -- Li<sub>2</sub> MnO<sub>3</sub> as a 3wt(s)% and electric conduction agent -- WO<sub>3</sub> 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- gamma-LiAlO<sub>2</sub> 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li<sub>1.33</sub>Ti<sub>1.67</sub>O<sub>4</sub> as 90wt(s)% and a solid electrolyte -- Li<sub>2</sub> TiO<sub>3</sub> as a 3wt(s)% and electric conduction agent -- WO<sub>3</sub> The laminating of the included negative-electrode Plastic solid which was included is carried out. 7wt(s)% -- All solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0038] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0039]

[The example 1 of a comparison] as positive active material -- LiMn<sub>2</sub>O<sub>4</sub> as a 93wt(s)% and electric conduction agent -- WO<sub>3</sub> 7wt(s)% -- the front face of the included positive-electrode sintered compact -- LiOH and MnO<sub>2</sub> applying -- the inside of air -- 375 degrees C -- 8 hours -- heat-treating -- Li<sub>2</sub> MnO<sub>3</sub> with a thickness of 10 micrometers The solid electrolyte layer was formed. The metal lithium negative electrode was stuck on the solid electrolyte layer, and all solid-state lithium secondary batteries were produced.

[0040] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0041] The configuration of the forward negative-electrode active material of examples 1-4 and the example 1 of a comparison and a solid electrolyte is collectively shown in Table 1.

[0042] All solid-state lithium secondary batteries were produced because insert in each component into a polyethylene ring with the outer diameter of 12mm, a bore [ of 11mm ], and a height of 220 micrometers and it pinches and carries out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.

[0043] It is 100microA/cm<sup>2</sup> about all the produced solid-state lithium secondary batteries. Charge-and-discharge capacity was measured with current density. The result is shown in Table 2.

[0044]

[Table 1]

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例 1	4 VLM	3 VLM	L 2 M	L 2 M	L 2 M
実施例 2	LNM	LT	L 2 M	L 2 M	L 2 T
実施例 3	4 VLM	3 VLM	L 2 M	L 2 T	L 2 M
実施例 4	LNM	LT	L 2 M	LA	L 2 T
比較例 1	LM	LM	— — —	L 2 M	— — —

ここで 4VLM:  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$

3VLM:  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$

LNM:  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$

LT:  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$

LM:  $\text{LiMn}_2\text{O}_4$

L 2 M:  $\text{Li}_2\text{MnO}_3$

L 2 T:  $\text{Li}_2\text{TiO}_3$

LA:  $\gamma\text{-LiAlO}_2$

[0045]

[Table 2]

試料	充放電電圧範囲 (V)	放電容量 (mAh/g) …正極基準	100 サイクル後の 容量保持率 (%)
実施例 1	0.0 ~ 2.0	75	89.0
実施例 2	2.5 ~ 4.5	76	91.5
実施例 3	0.0 ~ 2.0	81	90.1
実施例 4	2.5 ~ 4.5	85	92.9
比較例 1	3.0 ~ 4.3	69	65.0

[0046] as Table 2 showing — a solid electrolyte —  $\text{Li}_2\text{MnO}_3$   $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  with expansion contraction small to a positive electrode according a sintered compact to charge and discharge  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  with the expansion contraction small to a negative electrode by charge and discharge It is  $\text{Li}_2\text{MnO}_3$  to the used example 1 and a solid electrolyte. A sintered compact  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with the expansion contraction small to a positive electrode by charge and discharge  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  which does not have the expansion contraction by charge and discharge in a negative electrode The used example 2  $\text{LiMn}_2\text{O}_4$  which is a positive electrode It is solid electrolyte  $\text{Li}_2\text{MnO}_3$  to a sintered compact front face. The capacity retention after 100 cycles improved from the formed example 1 of a comparison.

[0047] Although the example 1 and the example 2 did not have abnormalities in the sample after charge-and-discharge measurement termination, in the example 1 of a comparison, it is weak and the powder considered that the positive electrode and the solid electrolyte were collapsed and generated was also checked.

[0048] Therefore, in the example 1 of a comparison, the expansion contraction at the time of the residual stress accompanying the lithium ion diffusion in the solid electrolyte which is not pressed down and charge and discharge is controlled in an example 1 and the example 2, the contact in the interface of solid electrolyte particles and the interface of an electrode and a solid electrolyte is not lost, but it is surmised that capacity degradation was also suppressed.

[0049] Furthermore, it is  $\text{Li}_2\text{TiO}_3$  as a solid electrolyte to the combination of the same forward negative electrode as an example 1. As for the example 3 using a sintered compact, an example 1 and the effectiveness more than equivalent were seen.

[0050] Furthermore, it is  $\gamma\text{-LiAlO}_2$  as a solid electrolyte to the combination of the same forward negative electrode as an example 2. As for the example 3 using a sintered compact, an example 2 and the effectiveness more than equivalent were seen.

[0051]

[Effect of the Invention] According to all the solid-state lithium secondary batteries concerning claim 1, a solid electrolyte As mentioned above,  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$  or  $\alpha\text{-LiAlO}_2$  From having formed with the sintered compact containing the lithium transition-metals multiple oxide which has the layer structure of at least one kind of rock salt mold inside A grain boundary will

exist in a solid electrolyte, the residual stress accompanying the lithium ion diffusion in a solid electrolyte particle is eased, and there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

[0052] Moreover, according to all the solid-state lithium secondary batteries concerning claim 2, it is a positive electrode  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  or  $(1.05 \leq x \leq 1.2) \text{Li}_x \text{Ni}_y \text{Mn}_{2-x-y} \text{O}_4$  of spinel type structure While forming with a sintered compact  $(1.0 \leq x \leq 1.2, 0.4 \leq y < 0.6)$  They are  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  of spinel type structure, or  $(1.25 \leq x \leq 1.40) \text{Li}_x \text{Ti}_{2-x} \text{O}_4$  about a negative electrode. From having formed with the sintered compact  $(1.25 \leq x \leq 1.40)$  Without spoiling contact of the interface of an electrode and a solid electrolyte, since it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem, there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

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TECHNICAL FIELD

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[Field of the Invention] Especially this invention relates to all the solid-state lithium secondary batteries that pinch a solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and are enclosed with it in a sheathing package about all solid-state lithium secondary batteries.

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to all the solid-state lithium secondary batteries concerning claim 1, a solid electrolyte As mentioned above,  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$  or  $\alpha\text{-LiAlO}_2$  From having formed with the sintered compact containing the lithium transition-metals multiple oxide which has the layer structure of at least one kind of rock salt mold inside A grain boundary will exist in a solid electrolyte, the residual stress accompanying the lithium ion diffusion in a solid electrolyte particle is eased, and there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

[0052] Moreover, according to all the solid-state lithium secondary batteries concerning claim 2, it is a positive electrode  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq x \leq 1.2)$   $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure While forming with a sintered compact  $(1.0 \leq x \leq 1.2, 0.4 \leq y < 0.6)$  They are  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  of spinel type structure, or  $(1.25 \leq x \leq 1.40)$   $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  about a negative electrode. From having formed with the sintered compact  $(1.25 \leq x \leq 1.40)$  Without spoiling contact of the interface of an electrode and a solid electrolyte, since it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem, there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

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[Translation done.]

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TECHNICAL PROBLEM

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[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device, and the cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.

[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.

[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has a problem of the rise of the internal resistance by a liquid spill of the electrolytic solution or deposit of the electrolytic-solution decomposition product in an active material front face.

[0005] In order to solve such a problem, development of all the solid-state lithium secondary batteries that do not use any electrolytic solution is considered.

[0006] JP,6-111831,A -- MnO<sub>2</sub> or a lithium compound is reacted to the front face of the positive electrode which consists of an alkali-metal manganese multiple oxide -- making -- Li<sub>2</sub>MnO<sub>3</sub> of a solid electrolyte Making it generate is advocated. According to this approach, since the adhesion of a positive electrode and a solid electrolyte is good, there is an advantage that interfacial resistance is low.

[0007] However, Li<sub>2</sub>MnO<sub>3</sub> Since it acts also as an active material which has charge and discharge potential in the 3V neighborhood, the very thing may check the charge-and-discharge reaction of a positive electrode, and the expansion contraction by the ejection and insertion of a lithium ion may also produce destruction of solid-state structure from a certain thing in that case, and, at this rate, it cannot serve as a solid electrolyte which can be used over a long period of time.

[0008] Furthermore, by JP,6-111831,A, when using a solid electrolyte, and an active material carries out expansion contraction at the time of the charge and discharge of an indispensable place, the method of avoiding the danger that the contact in the interface of an electrode and a solid electrolyte will be lost is not stated.

[0009] Moreover, in JP,6-275314,A, while using transition-metals oxide as a positive electrode, the lithium secondary battery which consists of a sulfide system lithium ion conductivity solid electrolyte with the ionic conductivity of bulk higher than an oxide system lithium ion conductivity solid electrolyte as a solid electrolyte is advocated.

[0010] However, since oxygen and the moisture of a minute amount decompose and a sulfide loses the work as a solid electrolyte, it has the fault that it can be hard to obtain a reliable cell.

[0011] This invention is made in view of the trouble of such a conventional technique, a solid electrolyte and an electrode carry out expansion contraction, and contact of the interface of a solid electrolyte and an electrode is spoiled, and it aims at offering all the solid-state lithium secondary batteries that canceled the conventional trouble that a solid electrolyte decomposed with oxygen and the moisture of a minute amount.

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MEANS

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[Means for Solving the Problem] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material in all the solid-state lithium secondary batteries concerning claim 1, and was enclosed with it in the sheathing package in order to attain the above-mentioned purpose, and they are  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{TiO}_3$ , or  $\alpha\text{-LiAlO}_2$  about said solid electrolyte. It is characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.

[0013] moreover, in all the solid-state lithium secondary batteries concerning claim 2 In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq X \leq 1.2)$   $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure While forming with a sintered compact  $(1.0 \leq X \leq 1.2, 0.4 \leq Y \leq 0.6)$  They are  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  of spinel type structure, or  $(1.25 \leq X \leq 1.40)$   $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  about said negative electrode. It is characterized by forming with a sintered compact  $(1.25 \leq X \leq 1.40)$ .  
[0014]

[Embodiment of the Invention] Hereafter, the operation gestalt of invention concerning each claim is explained. the sectional view showing the example of a configuration of all the solid-state lithium secondary batteries of invention which drawing 1 requires for claim 1 and claim 2 -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [ a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8 ] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.

[0015] In a solid electrolyte 5, it is  $\text{Li}_2\text{MnO}_3$ . Or  $\text{Li}_2\text{TiO}_3$  Or  $\alpha\text{-LiAlO}_2$  It uses. This solid electrolyte has the layer structure of a rock salt mold.

[0016] as the raw material which constitutes (1) solid-electrolyte fine particles or a solid electrolyte in order to produce a solid electrolyte 5 --  $\text{LiOH}$ ,  $\text{LiOH-H}_2\text{O}$ , and  $\text{Li}_2\text{CO}_3$  etc. -- with a lithium compound titanium compounds, such as manganese compounds, such as  $\text{MnO}$ ,  $\text{MnO}_2$ , and  $\text{MnOOH}$ , or  $\text{TiO}_2$ , or aluminum  $2\text{O}_3$  etc. -- with an aluminium compound How to judge and sinter, after distributing the water or the organic solvent in which the shaping assistant was dissolved, adjusting a slurry, carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) solid electrolytes or a solid electrolyte, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0017] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0018] The active material which consists of  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  or  $(1.05 \leq X \leq 1.2)$   $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  of spinel type structure  $(1.0 \leq X \leq 1.2, 0.4 \leq Y \leq 0.6)$  is used for a positive electrode 3.

[0019] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if X of  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$   $(1.05 \leq X \leq 1.2)$  is smaller than 1.05, and X is

larger than 1.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode will be spoiled.

[0020] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and  $\text{Li}_x \text{Ni}_y \text{Mn}_{2-x-y} \text{O}_4$  ( $1.0 \leq x \leq 1.2$ ,  $0.4 \leq y < 0.6$ ) will generate an impurity phase if sufficient high potential will not be obtained as compared with  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  ( $1.05 \leq x \leq 1.2$ ) if this  $y$  is smaller than 0.4, and  $y$  becomes 0.6 or more, it is not desirable.

[0021] The active material which consists of  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  of spinel type structure or ( $1.25 \leq x \leq 1.40$ )  $\text{Li}_x \text{Ti}_{2-x} \text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) is used for a negative electrode 6. The effectiveness of suppressing the expansion contraction at the time of charge and discharge if  $x$  of  $\text{Li}_x \text{Mn}_{2-x} \text{O}_4$  or ( $1.25 \leq x \leq 1.40$ )  $\text{Li}_x \text{Ti}_{2-x} \text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) is smaller than 1.25 here is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if  $x$  is larger than 1.4, it is not desirable.

[0022] The raw material which constitutes (1) active material, a solid electrolyte, or a solid electrolyte in order to produce a positive electrode 3 and a negative electrode 6, Distribute the water or the organic solvent in which the electric conduction agent and the shaping assistant were dissolved, and a slurry is adjusted. How to judge and sinter, after carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) active materials, a solid electrolyte, or a solid electrolyte, and an electric conduction agent, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0023] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0024] as the electric conduction agent added by a positive electrode 3 and the negative electrode 6 --  $\text{WO}_3$  etc. -- it is.

[0025] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material or a solid electrolyte, an active material, or a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.

[0026] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of electroconductive glue which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, contained conductive particles, such as gold, silver, copper, aluminum, nickel, and conductive carbon.

[0027] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as a terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0028] In order that the insulating section 4 may prevent the internal short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0029] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.

[0030]

[Example 1] as positive active material --  $\text{Li}_{1.1} \text{Mn}_{1.9} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  as a 3wt(s)% and electric conduction agent --  $\text{WO}_3$  7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material --  $\text{Li}_{1.33} \text{Mn}_{1.67} \text{O}_4$  as 90wt(s)% and a solid electrolyte --  $\text{Li}_2 \text{MnO}_3$  as a 3wt(s)% and electric conduction agent --  $\text{WO}_3$  7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0031] As for the size of all the produced solid-state lithium secondary battery components, for

the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0032]

[Example 2] as positive active material -- Li1.0 nickel0.5 Mn 1.5O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 MnO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Ti 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 TiO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0033] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0034] (What has what kind of the layer structure ?)

[0035]

[Example 3] as positive active material -- Li1.1 Mn 1.9O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 TiO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Mn 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0036] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0037]

[Example 4] as positive active material -- Li1.0 nickel0.5 Mn 1.5O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- gamma-LiAlO 2 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Ti 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 TiO3 as a 3wt(s)% and electric conduction agent -- WO3 The laminating of the included negative-electrode Plastic solid which was included is carried out. 7wt(s)% -- All solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0038] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0039]

[The example 1 of a comparison] as positive active material -- LiMn 2O4 as a 93wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the front face of the included positive-electrode sintered compact -- LiOH and MnO2 applying -- the inside of air -- 375 degrees C -- 8 hours -- heat-treating -- Li2 MnO3 with a thickness of 10 micrometers The solid electrolyte layer was formed. The metal lithium negative electrode was stuck on the solid electrolyte layer, and all solid-state lithium secondary batteries were produced.

[0040] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [ 10 micrometers and the negative electrode of phi10mm and thickness ] 100 micrometers.

[0041] The configuration of the forward negative-electrode active material of examples 1-4 and the example 1 of a comparison and a solid electrolyte is collectively shown in Table 1.

[0042] All solid-state lithium secondary batteries were produced because insert in each component into a polyethylene ring with the outer diameter of 12mm, a bore [ of 11mm ], and a height of 220 micrometers and it pinches and carries out thermocompression bonding to the

aluminum sheet metal of two sheets in an argon.

[0043] It is 100microA/cm<sup>2</sup> about all the produced solid-state lithium secondary batteries.

Charge-and-discharge capacity was measured with current density. The result is shown in Table 2.

[0044]

[Table 1]

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例 1	4VLM	3VLM	L2M	L2M	L2M
実施例 2	LNМ	LT	L2M	L2M	L2T
実施例 3	4VLM	3VLM	L2M	L2T	L2M
実施例 4	LNМ	LT	L2M	LA	L2T
比較例 1	LM	LM	— — —	L2M	— — —

ここで 4VLM:  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$

3VLM:  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$

LNМ:  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$

LT:  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$

LM:  $\text{LiMn}_2\text{O}_4$

L2M:  $\text{Li}_2\text{MnO}_3$

L2T:  $\text{Li}_2\text{TiO}_3$

LA:  $\gamma\text{-LiAlO}_2$

[0045]

[Table 2]

試料	充放電電圧範囲 (V)	放電容量 (mAh/g) …正極基準	100 サイクル後の 容量保持率 (%)
実施例 1	0.0 ~ 2.0	75	89.0
実施例 2	2.5 ~ 4.5	76	91.5
実施例 3	0.0 ~ 2.0	81	90.1
実施例 4	2.5 ~ 4.5	85	92.9
比較例 1	3.0 ~ 4.3	69	65.0

[0046] as Table 2 showing -- a solid electrolyte --  $\text{Li}_2\text{MnO}_3$   $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  with expansion contraction small to a positive electrode according a sintered compact to charge and discharge  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  with the expansion contraction small to a negative electrode by charge and discharge It is  $\text{Li}_2\text{MnO}_3$  to the used example 1 and a solid electrolyte. A sintered compact  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with the expansion contraction small to a positive electrode by charge and discharge  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  which does not have the expansion contraction by charge and discharge in a negative electrode The used example 2  $\text{LiMn}_2\text{O}_4$  which is a positive electrode It is solid electrolyte  $\text{Li}_2\text{MnO}_3$  to a sintered compact front face. The capacity retention after 100 cycles improved from the formed example 1 of a comparison.

[0047] Although the example 1 and the example 2 did not have abnormalities in the sample after charge-and-discharge measurement termination, in the example 1 of a comparison, it is weak and the powder considered that the positive electrode and the solid electrolyte were collapsed and generated was also checked.

[0048] Therefore, in the example 1 of a comparison, the expansion contraction at the time of the residual stress accompanying the lithium ion diffusion in the solid electrolyte which is not pressed down and charge and discharge is controlled in an example 1 and the example 2, the contact in the interface of solid electrolyte particles and the interface of an electrode and a solid electrolyte is not lost, but it is surmised that capacity degradation was also suppressed.

[0049] Furthermore, it is  $\text{Li}_2\text{TiO}_3$  as a solid electrolyte to the combination of the same forward negative electrode as an example 1. As for the example 3 using a sintered compact, an example 1 and the effectiveness more than equivalent were seen.

[0050] Furthermore, it is  $\gamma\text{-LiAlO}_2$  as a solid electrolyte to the combination of the same forward negative electrode as an example 2. As for the example 3 using a sintered compact, an

example 2 and the effectiveness more than equivalent were seen.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the example of a configuration of the coin type all solid-state lithium secondary battery in this invention.

[Description of Notations]

1 [ .. The insulating section (sheathing package), 5 / .. A solid electrolyte, 6 / .. A negative electrode, 7 / .. A negative-electrode current collection layer, 8 / .. Negative-electrode can (sheathing package) ] .... A positive-electrode can (sheathing package), 2 .. A positive-electrode current collection layer, 3 .. A positive electrode, 4

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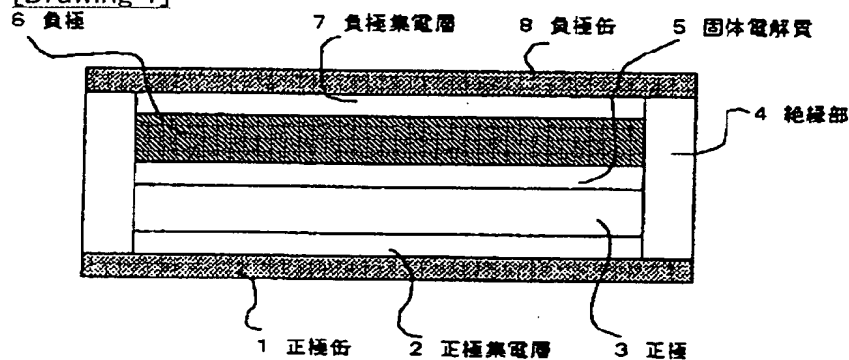
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DRAWINGS

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[Drawing 1]



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[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号  
特開2001-68149  
(P2001-68149A)

(43) 公開日 平成13年3月16日 (2001.3.16)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	テマコード (参考)
H 0 1 M 10/36		H 0 1 M 10/36	A 5 H 0 0 3
4/02		4/02	A 5 H 0 1 4
4/58		4/58	5 H 0 2 9

審査請求 未請求 請求項の数 2 O L (全 6 頁)

(21) 出願番号 特願平11-244040

(22) 出願日 平成11年8月30日 (1999.8.30)

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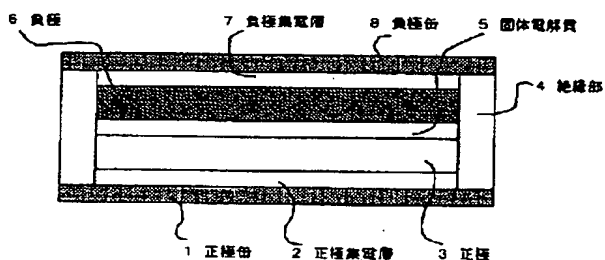
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(54) 【発明の名称】 全固体リチウム二次電池

(57) 【要約】

【課題】 固体電解質や電極が膨脹収縮して固体電解質と電極との界面の接触が損なわれ、また固体電解質が微量の酸素や水分によって分解するという問題があった。

【解決手段】 活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質を  $\text{Li}_2\text{MnO}_3$ 、 $\text{Li}_2\text{TiO}_3$ 、または  $\alpha\text{-LiAlO}_2$  のうち少なくとも1種類の層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする。



## 【特許請求の範囲】

【請求項 1】 活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質を  $\text{Li}_2\text{MnO}_3$ 、 $\text{Li}_2\text{TiO}_3$ 、または  $\alpha\text{-LiAlO}_2$  のうち少なくとも 1 種類の岩塩型層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする全固体リチウム二次電池。

【請求項 2】 活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記正極をスピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq X \leq 1.2$ ) または  $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  ( $1.0 \leq X \leq 1.2$ ,  $0.4 \leq Y < 0.6$ ) 焼結体で形成するとともに、前記負極をスピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.25 \leq X \leq 1.4$ ) または  $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  ( $1.25 \leq X \leq 1.4$ ) 焼結体で形成したことを特徴とする全固体リチウム二次電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は全固体リチウム二次電池に関し、特に活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入する全固体リチウム二次電池に関する。

## 【0002】

【従来の技術および発明が解決しようとする課題】 近年のノートパソコンや携帯電話等の携帯用電子機器の高性能化と小型化にはめざましいものがあり、これら携帯機器に使用される電池では、より一層の高エネルギー密度化と小型化が要求されている。

【0003】 このような要求に応えるものとして、リチウムイオンの脱挿入を利用したリチウム二次電池が盛んに研究されている。

【0004】 しかしながら、従来のリチウム二次電池は非水電解液を使用していることから、電解液の漏液、あるいは活物質表面における電解液分解生成物の析出による内部抵抗の上昇といった問題がある。

【0005】 このような問題を解決するために、電解液を一切使わない全固体リチウム二次電池の開発が検討されている。

【0006】 例えば特開平 6-111831 号公報では、 $\text{MnO}_2$  またはアルカリ金属マンガン複合酸化物からなる正極の表面に、リチウム化合物を反応させて固体電解質の  $\text{Li}_2\text{MnO}_3$  を生成させることが提唱されている。この方法によれば、正極と固体電解質の密着性が良いため、界面抵抗が低いという利点がある。

【0007】 しかしながら、 $\text{Li}_2\text{MnO}_3$  自体は 3V 付近に充放電電位を有する活物質としても作用することから、正極の充放電反応を阻害する可能性があり、またその際にリチウムイオンの脱挿入による膨脹収縮もある

ことから、固体構造の破壊を生じる可能性があり、このままでは長期にわたって使用できる固体電解質とはなり得ない。

【0008】 さらに、特開平 6-111831 号公報では、固体電解質を用いる場合には必須であるところの、充放電時に活物質が膨脹収縮することによって電極と固体電解質との界面における接触が失われる危険性を回避する方法については述べられていない。

【0009】 また、特開平 6-275314 号公報では、正極として遷移金属酸化物を用いるとともに、固体電解質として酸化物系リチウムイオン伝導性固体電解質よりもバルクのイオン伝導度が高い硫化物系リチウムイオン伝導性固体電解質とからなるリチウム二次電池が提唱されている。

【0010】 しかしながら、硫化物は微量の酸素や水分により分解して固体電解質としての働きを失うため、信頼性の高い電池を得られにくいという欠点がある。

【0011】 本発明はこのような従来技術の問題点に鑑みてなされたものであり、固体電解質や電極が膨脹収縮して固体電解質と電極との界面の接触が損なわれ、また固体電解質が微量の酸素や水分によって分解するという従来の問題点を解消した全固体リチウム二次電池を提供することを目的とする。

## 【0012】

【課題を解決するための手段】 上記目的を達成するために、請求項 1 に係る全固体リチウム二次電池では、活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質を  $\text{Li}_2\text{MnO}_3$ 、 $\text{Li}_2\text{TiO}_3$ 、または  $\alpha\text{-LiAlO}_2$  のうち少なくとも 1 種類の岩塩型層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする。

【0013】 また、請求項 2 に係る全固体リチウム二次電池では、活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記正極をスピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq X \leq 1.2$ ) または  $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  ( $1.0 \leq X \leq 1.2$ ,  $0.4 \leq Y < 0.6$ ) 焼結体で形成するとともに、前記負極をスピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.25 \leq X \leq 1.4$ ) または  $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  ( $1.25 \leq X \leq 1.4$ ) 焼結体で形成したことを特徴とする。

## 【0014】

【発明の実施の形態】 以下、各請求項に係る発明の実施形態を説明する。図 1 は請求項 1 および請求項 2 に係る発明の全固体リチウム二次電池の構成例を示す断面図であり、1 は正極缶、2 は正極集電層、3 は正極、4 は絶縁部、5 は固体電解質、6 は負極、7 は負極集電層、8 は負極缶である。正極缶 1 と負極缶 8 と絶縁部 4 とで外装パッケージが構成される。

【0015】固体電解質5には、 $\text{Li}_2\text{MnO}_3$  または  $\text{Li}_2\text{TiO}_3$  または  $\alpha\text{-LiAlO}_2$  を用いる。この固体電解質は岩塩型の層状構造を有する。

【0016】固体電解質5を作製するには、(1) 固体電解質粉体、または固体電解質を構成する原料として  $\text{LiOH}$ 、 $\text{LiOH}\cdot\text{H}_2\text{O}$ 、 $\text{Li}_2\text{CO}_3$  などのリチウム化合物と、 $\text{MnO}$ 、 $\text{MnO}_2$ 、 $\text{MnOOH}$ などのマンガ化合物、または  $\text{TiO}_2$ などのチタン化合物、または  $\text{Al}_2\text{O}_3$ などのアルミニウム化合物と、成形助剤とを溶解させた水または有機溶剤に分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、あるいは、(2) 固体電解質または固体電解質を構成する原料を直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【0017】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの1種もしくは2種以上の混合物が挙げられる。

【0018】正極3には、スピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq x \leq 1.2$ ) または  $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  ( $1.0 \leq x \leq 1.2$ ,  $0.4 \leq y < 0.6$ ) から成る活物質を用いる。

【0019】ここで、 $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq x \leq 1.2$ ) の  $x$  が  $1.05$  より小さいと充放電時の膨脹収縮を抑える効果が十分でなく、また  $x$  が  $1.2$  より大きいと充放電容量の低下が顕著であるため、正極に用いる利点が損なわれる。

【0020】また、 $\text{Li}_x\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  ( $1.0 \leq x \leq 1.2$ ,  $0.4 \leq y < 0.6$ ) はより高電位の正極材料であるが、この  $y$  が  $0.4$  より小さいと  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq x \leq 1.2$ ) に比較して十分な高電位が得られず、また  $y$  が  $0.6$  以上になると  $\text{Ni}$  が固溶しきらず、不純物相を生成するので好ましくない。

【0021】負極6には、スピネル型構造の  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) または  $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) から成る活物質を用いる。ここで  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) または  $\text{Li}_x\text{Ti}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) の  $x$  が  $1.25$  より小さいと、充放電時の膨脹収縮を抑える効果が充分でなく、また  $x$  が  $1.4$  より大きいとリチウムが固溶しきらず、不純物相を生成するので好ましくない。

【0022】正極3および負極6を作製するには、

(1) 活物質、固体電解質または固体電解質を構成する原料、導電剤、および成形助剤とを溶解させた水または有機溶剤に分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、

あるいは(2) 活物質、固体電解質または固体電解質を構成する原料、および導電剤とを直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【0023】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの1種もしくは2種以上の混合物が挙げられる。

【0024】正極3および負極6に添加される導電剤としては  $\text{WO}_3$  などがある。

【0025】固体電解質5、正極3、および負極6の焼結条件は、 $500^\circ\text{C}$  から  $900^\circ\text{C}$  で30分から30時間の範囲内で、活物質または固体電解質の組成、活物質または固体電解質の合成条件、あるいは焼結体のサイズに応じて適宜選択される。

【0026】正極集電層2および負極集電層7は、正極缶1と正極3、あるいは負極缶8と負極6との接触と集電のために配置され、例えば金、銀、銅、アルミニウム、ニッケル、導電性カーボンなどの導電性粒子を含んだ導電性接着剤からなる。

【0027】正極缶1および負極缶8は、大気中の水分による充放電反応の阻害を防ぐため、および正極3と負極6の端子として用いるために配置され、例えばアルミニウム、銅、ニッケル、ステンレススチール、チタンなどの金属の薄板が用いられる。

【0028】絶縁部4は、正極3と負極6との内部短絡を防ぐために配置され、例えばポリエチレン、ポリプロピレン、ポリイミドなどの高分子が用いられる。

【0029】正極缶1、絶縁部4、および負極缶8とで外装パッケージが構成される。

【0030】

【実施例1】正極活物質として  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  を90wt%、固体電解質として  $\text{Li}_2\text{MnO}_3$  を3wt%、導電剤として  $\text{WO}_3$  を7wt%含んだ正極成形体と、固体電解質として  $\text{Li}_2\text{MnO}_3$  を100wt%含んだ固体電解質成形体と、負極活物質として  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  を90wt%、固体電解質として  $\text{Li}_2\text{MnO}_3$  を3wt%、導電剤として  $\text{WO}_3$  を7wt%含んだ負極成形体を積層して、 $750^\circ\text{C}$  で20時間処理することにより全固体リチウム二次電池素子を作製した。

【0031】作製した全固体リチウム二次電池素子のサイズは  $\phi 10\text{mm}$ 、厚さは正極が  $100\mu\text{m}$ 、固体電解質が  $10\mu\text{m}$ 、負極が  $100\mu\text{m}$  であった。

【0032】

【実施例2】正極活物質として  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  を90wt%、固体電解質として  $\text{Li}_2\text{MnO}_3$  を3wt%、導電剤として  $\text{WO}_3$  を7wt%含んだ正極成形体と、固体電解質として  $\text{Li}_2\text{MnO}_3$  を100wt%含んだ固体電解質成形体と、負極活物質として  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  を90wt%、固体電解質として  $\text{Li}_2\text{MnO}_3$  を3wt%、導電剤として  $\text{WO}_3$  を7wt%含んだ負極成形体を積層して、 $750^\circ\text{C}$  で20時間処理することにより全固体リチウム二次電池素子を作製した。

$\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  を 90 wt %、固体電解質として  $\text{Li}_2\text{TiO}_3$  を 3 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ負極成形体を積層して、750℃で20時間処理することにより全固体リチウム二次電池素子を作製した。

【0033】作製した全固体リチウム二次電池素子のサイズはφ10mm、厚さは正極が100μm、固体電解質が10μm、負極が100μmであった。

【0034】(何がどのような層状構造になっている?)

【0035】

【実施例3】正極活物質として  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  を 90 wt %、固体電解質として  $\text{Li}_2\text{MnO}_3$  を 3 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ正極成形体と、固体電解質として  $\text{Li}_2\text{TiO}_3$  を 100 wt % 含んだ固体電解質成形体と、負極活物質として  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  を 90 wt %、固体電解質として  $\text{Li}_2\text{MnO}_3$  を 3 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ負極成形体を積層して、750℃で20時間処理することにより全固体リチウム二次電池素子を作製した。

【0036】作製した全固体リチウム二次電池素子のサイズはφ10mm、厚さは正極が100μm、固体電解質が10μm、負極が100μmであった。

【0037】

【実施例4】正極活物質として  $\text{Li}_{1.6}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  を 90 wt %、固体電解質として  $\text{Li}_2\text{MnO}_3$  を 3 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ正極成形体と、固体電解質として  $\gamma\text{-LiAlO}_2$  を 100 wt % 含んだ固体電解質成形体と、負極活物質として  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  を 90 wt %、固体電解質として\*30

\*  $\text{Li}_2\text{TiO}_3$  を 3 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ含んだ負極成形体を積層して、750℃で20時間処理することにより全固体リチウム二次電池素子を作製した。

【0038】作製した全固体リチウム二次電池素子のサイズはφ10mm、厚さは正極が100μm、固体電解質が10μm、負極が100μmであった。

【0039】

【比較例1】正極活物質として  $\text{LiMn}_2\text{O}_4$  を 93 wt %、導電剤として  $\text{WO}_3$  を 7 wt % 含んだ正極焼結体の表面に  $\text{LiOH}$  と  $\text{MnO}_2$  を塗布し、空気中にて375℃で8時間熱処理して、厚さ10μmの  $\text{Li}_2\text{MnO}_3$  固体電解質層を形成した。固体電解質層の上に金属リチウム負極を貼りつけて、全固体リチウム二次電池を作製した。

【0040】作製した全固体リチウム二次電池素子のサイズはφ10mm、厚さは正極が100μm、固体電解質が10μm、負極が100μmであった。

【0041】実施例1～4、比較例1の正負極活物質、固体電解質の構成について表1にまとめて示す。

【0042】各々の素子をアルゴン中にて、外径12mm、内径11mm、高さ220μmのポリエチレンリング中にはめ込み、二枚のアルミニウム薄板に挟んで熱圧着することで全固体リチウム二次電池を作製した。

【0043】作製した全固体リチウム二次電池について100μA/cm<sup>2</sup>の電流密度で充放電容量を測定した。その結果を表2に示す。

【0044】

【表1】

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例1	4VLM	3VLM	L2M	L2M	L2M
実施例2	LNМ	LT	L2M	L2M	L2T
実施例3	4VLM	3VLM	L2M	L2T	L2M
実施例4	LNМ	LT	L2M	LA	L2T
比較例1	LM	LM	— — —	L2M	— — —

ここで 4VLM:  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$

3VLM:  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$

LNМ:  $\text{Li}_{1.6}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$

LT:  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$

LM:  $\text{LiMn}_2\text{O}_4$

L2M:  $\text{Li}_2\text{MnO}_3$

L2T:  $\text{Li}_2\text{TiO}_3$

LA:  $\gamma\text{-LiAlO}_2$

【0045】

【表2】

試料	充放電電圧範囲 (V)	放電容量 (mAh/g) …正極基準	100 サイクル後の 容量保持率 (%)
実施例 1	0.0 ~ 2.0	75	89.0
実施例 2	2.5 ~ 4.5	76	91.5
実施例 3	0.0 ~ 2.0	81	90.1
実施例 4	2.5 ~ 4.5	85	92.9
比較例 1	3.0 ~ 4.3	69	65.0

【0046】表2からわかる通り、固体電解質に  $\text{Li}_2\text{MnO}_3$  焼結体を、正極に充放電による膨脹収縮の小さい  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  を、負極に充放電による膨脹収縮の小さい  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  を用いた実施例1、および固体電解質に  $\text{Li}_2\text{MnO}_3$  焼結体を、正極に充放電による膨脹収縮の小さい  $\text{Li}_{1.0}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  を、負極に充放電による膨脹収縮のない  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  を用いた実施例2は、正極である  $\text{LiMn}_2\text{O}_4$  焼結体表面に固体電解質  $\text{Li}_2\text{MnO}_3$  を形成した比較例1より100サイクル後の容量保持率が向上した。

【0047】実施例1および実施例2は充放電測定終了後のサンプルに異常はなかったが、比較例1では脆くなっており、正極および固体電解質が崩れて発生したと思われる粉も確認された。

【0048】したがって、比較例1では抑えられていない固体電解質中のリチウムイオン拡散に伴う残留応力と充放電時の膨脹収縮が、実施例1および実施例2では抑制され、そのため固体電解質粒子同士の界面および電極と固体電解質との界面における接触が失われず、容量劣化も抑えられたと推測される。

【0049】さらに、実施例1と同じ正負極の組み合わせに、固体電解質として  $\text{Li}_2\text{TiO}_3$  焼結体を用いた実施例3は、実施例1と同等以上の効果が見られた。

【0050】さらに、実施例2と同じ正負極の組み合わせに、固体電解質として  $\gamma\text{-LiAlO}_2$  焼結体を用いた実施例3は、実施例2と同等以上の効果が見られた。

【0051】

【発明の効果】以上のように、請求項1に係る全固体リチウム二次電池によれば、固体電解質を  $\text{Li}_2\text{Mn}$

$\text{O}_3$ 、 $\text{Li}_2\text{TiO}_3$ 、または  $\alpha\text{-LiAlO}_2$  のうち少なくとも1種類の岩塩型の層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことから、固体電解質中に粒界が存在することになり、固体電解質粒子中のリチウムイオン拡散に伴う残留応力が緩和され、長期にわたって内部抵抗の劣化が無く、したがって容量劣化の少ない電池を提供することができる。

【0052】また、請求項2に係る全固体リチウム二次電池によれば、正極をスピネル型構造の  $\text{Li}_i\text{Mn}_{2-x}\text{O}_4$  ( $1.05 \leq x \leq 1.2$ ) または  $\text{Li}_i\text{Ni}_y\text{Mn}_{2-x-y}\text{O}_4$  ( $1.0 \leq x \leq 1.2$ 、 $0.4 \leq y < 0.6$ ) 焼結体で形成するとともに、負極をスピネル型構造の  $\text{Li}_i\text{Mn}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) または  $\text{Li}_i\text{Ti}_{2-x}\text{O}_4$  ( $1.25 \leq x \leq 1.40$ ) 焼結体で形成したことから、これら活物質の充放電時の膨脹収縮が全くないかあるいはほとんど問題にならない程度に小さいため、電極と固体電解質との界面の接触が損なわれることなく、長期にわたって内部抵抗の劣化が無く、したがって容量劣化の少ない電池を提供することができる。

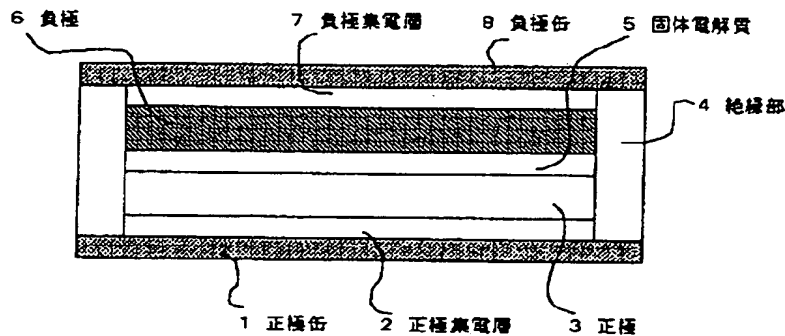
【図面の簡単な説明】

【図1】本発明におけるコイン型全固体リチウム二次電池の構成例を示す断面図である。

【符号の説明】

1 ……正極缶 (外装パッケージ)、2 ……正極集電層、3 ……正極、4 ……絶縁部 (外装パッケージ)、5 ……固体電解質、6 ……負極、7 ……負極集電層、8 ……負極缶 (外装パッケージ)

【図1】



【手続補正書】

【提出日】平成11年9月3日(1999. 9. 3)

\* 【補正対象項目名】0034

【手続補正1】

【補正方法】削除

【補正対象書類名】明細書

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Fターム(参考) 5H003 AA00 BB05 BC05 BC06 BD00  
5H014 AA01 AA06 EE10 HH00  
5H029 AJ00 AJ14 AK03 AL03 AM12  
BJ03 BJ04 DJ17 HJ02 HJ13